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Part II

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

HIGH DOSE INTEGRATING CHEMICAL DOSIMETERS

The radiolysis of aqueous sodium oxalate solutions

by

G. JUPPE, H. KOLMAR and R. FANTECHI

1968

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Organic Chemistry

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SUMMARY

The radiolytic decomposition of aqueous 0.1 N, 0.2 N and 0.4 N sodium oxalate solutions was studied using 2 MV electrons from a van de Graaff accelerator. High dose rates (0.2×10^6 rad/sec) were achieved and conversions of the starting material of higher than 99 % finally obtained.

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KEYWORDS

RADIOLYSIS
SOLUTIONS
WATER
SODIUM COMPOUNDS
OXALATES
ELECTRON BEAMS
REACTION KINETICS
CARBON DIOXIDE

G-value

CONTENTS

HIGH DOSE INTEGRATING CHEMICAL DOSIMETERS
The Radiolysis of Aqueous Sodium Oxalate Solution (+)

1. - I N T R O D U C T I O N

Aqueous solutions of oxalic acid have been considered for use as high dose integrating dosimeters for in-pile dosimetry.

I.Draganic[1] studied the influence of different radiation parameters, like temperature, dose rate, pH-effects, total dose and initial concentration of the starting material and discussed the mechanism of the radiolysis.

The decrease in oxalic acid after in-pile irradiations (reflector of the EL-2-reactor, Saclay, France) or after radiolysis by gamma rays from a 7o curie ^{60}Co-source was analytically determined by photospectroscopy of the cupri-benzidine complex formed with oxalic acid. Better reproducible values were obtained by manganometric titration of oxalic acid.

As reaction products hydrogen, carbon dioxide, formaldehyde and glyoxal were observed. I.Draganic[2] determined at pH lower than 2 and at initial oxalic acid concentrations of 25 mM or higher the following G-values for decompositions of less than 3o% of the starting material:

$$G_{\text{oxalic acid}} = -4.9$$
$$G_{CO_2} = 7.8$$
$$G_{\text{hydrogen}} = o.46$$
$$G_{\text{formaldehyde}} = o.o8$$
$$G_{\text{glyoxal}} = o.oo4$$

No oxygen, carbon monoxide, formic acid, acetic acid, glyoxylic acid, mesoxalic acid or dioxoglutaric acid were found. The methods of analysis for the latter compounds were capable of detecting concentrations of less than o.o1%.

(+) Manuscript received on March 1. 1968.

No influence of the dose rate between 0.2 and 110 rad/sec and of the temperature between 20°C and 80°C was noted. At pH < 2 equal amounts of oxalic acid decreased both in aerated and deaerated solutions.

The G-value for the oxalic acid decrease was found to be strongly pH-dependent. In 10 to 100 mM solutions and in a pH range between zero and two a G-value of 4.9 was established for the oxalic acid decrease. At pH 5, pH 10, and pH 14 smaller G-values were observed being 1.9, 1.6, and 0.3, respectively.

M.Matsui[3] reported a strong dependence of the G-value for the oxalic acid decrease from the initial concentration of the starting material. At 0.2×10^6 rad absorption a G-value of 5.24 was noted for an initial concentration of 12×10^{18} molecules and a G-value of 7.33 was found for an initial concentration of 74×10^{18} molecules oxalic acid in the starting solution. Also a rather large dependence from the total dose absorbed was observed. After 0.2×10^6 rad absorption 5.24 molecules of oxalic acid per 100 eV had disappeared. After 11.2×10^6 rads absorption a G-value of only 1.9 was observed. Both solutions contained 12.1×10^{18} molecules of oxalic acid before the radiolysis.

A rather large LET dependence for the oxalic acid radiolysis was found. The G-value for the decrease in starting material, being in the pH-range zero to two 4.9 for the gamma radiolysis, became under comparable experimental conditions for low energy proton irradiation 0.3 to 0.7. Also here the yield decreased with decreasing concentration, decreasing energy and increasing dose rates.

A reaction mechanism explaining the product formation in both acid and alkaline medium was proposed by I.Draganic and M.T.Nenadovic[4]. At pH higher than 6, where oxalic acid is completely dissociated, the primarily formed $H^{\cdot}$, $OH^{\cdot}$ radicals and solvated electrons, originating from the water radiolysis, should be responsible for the following reaction steps:

$$(COO)_2^{--} + OH^{\cdot} \longrightarrow OH^- + CO_2 + (COO)$$

$$+ H^{\cdot} \xrightarrow{H_2O} 2\ OH^- + CO_2 + CHO$$

$$+ H_2O^- \xrightarrow{H_2O} 3\ OH^- + CO_2 + CHO$$

Consecutive reactions of carbon dioxide, this being an efficient acceptor for solvated electrons, might lead to

$$CO_2 + OH \longrightarrow HCO_3$$

$$+ H \longrightarrow COOH$$

$$+ H_2O^- \longrightarrow COO^- + H_2O$$

In the investigations hitherto performed low dose rates and rather low oxalic acid conversions were chosen. In the present work the radiolysis of sodium oxalate in alkaline solution, high dose rates ($0.2 \cdot 10^6$ rad/sec) and high initial concentrations (0.1 to 0.4 M/l) were used. Conversions of the starting material higher than 99% were finally obtained.

2. - MATERIALS AND METHODS

2.1 - MATERIALS

All chemicals used were analytical grade. The water used had been distilled from alkaline permanganate and redistilled in a quartz apparatus. The o.1, o.2 and o.4 N sodium oxalate solutions were nitrogen purged before use.

2.2 - IRRADIATIONS

The source of radiation was a 2 MeV/25o/uA van de Graaff electron accelerator (High Voltage Engineering (Europe), Amersfoort, Holland). Both the stainless steel irradiation cell and the irradiation procedure have been described before[5]. Dosimetry of the irradiation system had been performed by using the reductant formation (G = 3.63) from the radiolysis of o.1 sodium formate solutions at an identical voltage setting. The dose rate was o.2 x 10^5 rad/sec. The results of the dosimetry are tabulated in table 1 and illustrated in fig. 1.

TABLE 1 FORMATE DOSIMETRY

(o.1 N aqueous sodium formate, 1.5 MV, 1oo/uA)

IRRADIATION TIME (sec)	CONSUMPTION $KMnO_4$ (mEq/5o ml)	DOSE ABSORBED (10^6 rad)
o	o	o
5o	1.58	8.35
1oo	3.14	16.7
15o	4.61	25
175	4.82	29.2

2.3 - ANALYSIS

The experimental technique used for the determination of the reductants present in the irradiated sample, in acid and in alkaline solution, and the acidimetric determinations of the total of carboxy groups disappeared during the radiolysis and the carboxy groups being transformed into neutral substituents have been described before[5].

2.4 - ISOLATION OF RADIOLYSIS PRODUCTS

2.4.1 - SEPARATION OF NEUTRAL COMPOUNDS

50 ml of 0.4 N aqueous sodium formate solution were irradiated until 500 x 10^6 rad had been absorbed. The alkaline solution was then perforated with ether for 90 hours at room temperature. Negligible amounts of liquid residue were found after the ether removal. The small amounts isolated did not allow an identification of the components of this product mixture.

2.4.2 - SEPARATION OF ACIDS

The ether perforation of the irradiated solution was continued after acidifying the solution with 4 N sulfuric acid. After the evaporation of the ether solvent 415 mg of solid residue remained. The product had a m.p. of 190-91°C. The m.p. of a pure sample of oxalic acid was 191-92°C. No depression was noted when mixing the two compounds.

The column chromatography for separating oxalic acid from other acidic reaction products on silica has been described before[5].

3. - R E S U L T S

3.1 - TOTAL DOSE AND INITIAL OXALATE CONCENTRATION DEPENDENCE

3.1.1 - DEPENDENCE OF REDUCTANT CONCENTRATION FROM THE DOSE ABSORBED

50 ml of 0.1, 0.2 and 0.4 N aqueous sodium oxalate solutions were irradiated up to a total dose of 250 x 10^6 rad, 400 x 10^6 rad and 500 x 10^6 rad, respectively.

The concentrations of permanganate-reducing compounds being present in the initially 0.1 N solution and oxidized in acid solution are listed in table 2 and are illustrated in fig. 2.

TABLE 2 REDUCTANT CONCENTRATIONS AFTER RADIOLYSIS OF 0.1 N SODIUM OXALATE SOLUTIONS (50 ml solution) (TITRATION IN ACID MEDIUM)

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	2nd R_a-VALUE*) mEq $KMnO_4$/50 ml solution
0	0	4.92
125	25	4.04
250	50	3.32
375	75	2.52
500	100	2.14
625	125	1.35
750	150	0.60
1000	200	0.18
1250	250	0.05

*) The reaction solution was titrated to a point where the permanganate colour remained for appr. 10 seconds (1st R_a-value). The titration was then continued until the permanganate was not decolorized for more than 120 seconds (2nd R_a-value). The first R_a- value stands for the number of oxalic acid equivalents; the second R_a-value gives also a rough measure of other acids present with the exception of formic acid, which is not oxidized under these conditions.

The concentrations of permanganate-reducing compounds in acid solution, after radiolyzing a o.2 N sodium oxalate solution are listed in table 3.

TABLE 3 REDUCTANT CONCENTRATIONS AFTER RADIOLYSIS OF o.2 N SODIUM OXALATE SOLUTIONS (5o ml solution) (TITRATION IN ACID MEDIUM)

IRRADIATION TIME (sec)	TOTAL DOSE ($1o^6$ rad)	2^{nd} R_a-VALUE*) (mE_q $KMnO_4$/5o ml)
o	o	9.91
25o	5o	7.52
5oo	1oo	5.29
75o	15o	3.65
1ooo	2oo	2.26
1125	225	1.66
1125	225	1.87
125o	25o	o.73
125o	25o	o.35
1375	275	o.6o

*) Decolorisation of permanganate only after 12o sec.

In fig. 3 are also compared the titration values of the permanganate oxidation in acid medium of the o.1 N and o.2 N sodium oxalate solutions.

The concentrations of permanganate-reducing compounds in acid solution, after the radiolysis of a o.4 N sodium oxalate solution, are listed in table 4.

TABLE 4 REDUCTANT CONCENTRATIONS AFTER RADIOLYSIS OF A o.4 N SODIUM OXALATE SOLUTION (5o ml sample) (TITRATION IN ACID MEDIUM)

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	1st R_a-VALUE (mEq $KMnO_4$/5o ml)	2nd R_a-VALUE (mEq $KMnO_4$/5o ml)
o	o	2o.35	2o.35
25o	5o	17.2o	17.6
5oo	1oo	14.55	15.15
75o	15o	12.7o	13.4
1ooo	2oo	11.25	11.8
15oo	3oo	7.9	8.25
15oo	3oo	7.6	8.o
2ooo	4oo	4.25	4.25
25oo	5oo	1.1	1.1
25oo	5oo	o.o4	o.o4

The concentrations of permanganate-reducing compounds in alkaline solution, after radiolyzing a o.4 N sodium oxalate solution are listed in table 5. The permanganate equivalents consumed (R_b-values) are a direct measure of all reducing compounds in solution including formate, and other anions not being oxidized in acidic solution.

TABLE 5 REDUCTANT CONCENTRATION AFTER THE RADIOLYSIS OF o.4 N SODIUM OXALATE SOLUTIONS (5o ml sample) TITRATION IN ALKALINE MEDIUM

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	R_b-VALUE (mEq $KMnO_4$/5o ml solution)
o	o	2o.55
25o	5o	17.7o
75o	15o	13.25
15oo	3oo	7.95

Fig. 4 summarizes the results of the acid and alkaline oxidations for the o.4 N sodium oxalate solution.

3.1.2 - DEPENDENCE OF ACID CONCENTRATIONS FROM THE DOSE ABSORBED

The results of the acid base titrations of an irradiated o.4 N sodium oxalate solution with or without previous removal of carbonate (carbon dioxide) from the samples are listed in table 6 and illustrated in fig. 5*). The values for the

*) The radiolytic decomposition of aqueous sodium oxalate solution leads to the formation of hydroxyl ions:

$$2\ H_2O + (COO^-)_2 \rightarrow 2\ CO_2 + 2\ OH^-\ (COO^-)_2$$

Compared with the initial pH a stronger alkaline reaction is observed. The titration with mineral acid leads to the determination of the total hydroxide (H_t-values).
By addition of barium chloride to the irradiated solution carbon dioxide is removed:

$$CO_2 + OH^- + BaCl_2 \rightarrow BaCO_3 + 2\ Cl^- + H^+$$

For equal amounts of hydroxyl and carbon dioxide an acid reaction is obtained. The titration with a o.1 N base leads then to the determination of the "free hydroxide" (H_f-value).
Only for a complete destruction of oxalate a 1:1 ratio for the carbon dioxide-hydroxyl anion formation is achieved and then H_f should equal - H_t. For partial destruction this ratio is in favor of a higher OH^- content.

total hydroxide (H_t-values) are a direct measure of the number of -COOH groups destroyed during the radiolysis. The difference between the total hydroxide values (H_t-values) and the free hydroxide values (H_f-values) is due to the formation of carbon dioxide during the radiolysis.

TABLE 6 RADIOLYSIS OF o.4 N SODIUM OXALATE ACID BASE TITRATIONS

IRRADIATION TIME (sec)	TOTAL DOSE (10^6 rad)	FREE HYDROXIDE H_f (mEq/5o ml solution)	TOTAL HYDROXIDE H_t (mEq/5o ml solution)
o	o	o.o	o.o
25o	5o	- 2.5	3.2
5oo	1oo	- 4.65	5.85
75o	15o	- 6.55	7.85
1ooo	2oo	- 7.95	9.15
15oo	3oo	-11.5o	12.45
15oo	3oo	-11.2	12.35
2ooo	4oo	-14.55	15.75
25oo	5oo	-17.65	18.85
25oo	5oo	-18.6	2o.25

For two hydroxyl anions per carbon dioxide formed a neutral pH is for instance reached after barium chloride addition

$$CO_2 + 2\ OH^- + BaCl_2 \longrightarrow BaCO_3 + 2\ Cl^- + H_2O$$

4. - DISCUSSION OF THE RESULTS

4.1 - OXALATE DECREASE

4.1.1 - LOW INITIAL OXALATE CONCENTRATIONS

4.1.1.1 - REACTION ORDER

The manganametric titration in acid solution leads to the oxidation of oxalic acid and radiolysis products being oxidized under these conditions. The predominant component in the solutions even after prolonged radiolysis time is, nevertheless, oxalate. The R_a-values, i.e. the number of permanganate equivalents used during the titration can therefore be taken as a rough measure for the oxalate concentration.

Linearity for the decrease in oxalic acid of a o.1 N and o.2 N solution up to 225×10^6 rad absorption is obtained when plotting the square root of the R_a-values versus the absorbed dose or the irradiation time indicating a o.5 reaction order (fig. 6). A value of 3.32×10^{-3} (sec^{-1}) for the rate constant can be calculated from this figure. The following equations hold:

$$\frac{dc}{dt} = - k \sqrt{c}$$

$$\sqrt{c} = \sqrt{c_o} - \frac{1}{2} kt$$

For the initially o.1 N sodium oxalate solution, we have

$$\sqrt{R_a} = 3.15 - (1.66 \times 10^{-3})\ t.$$

In these equations c_o is the initial concentration of oxalate, and c the concentration at time t (seconds); c, c_o, and R_a are expressed in mEq/5o ml.

Due to the linearity between irradiation time (t) and dose (D megarads) we have also:

$$\sqrt{R_a} = 3.15 - (8.3 \times 10^{-3})D$$

The value 3.15 appearing in the last two equations is equal to $\sqrt{9.91}$, that is the root of the initial concentration of oxalate (fig. 3 and 6).

4.1.1.2 - G-VALUE

If the solution contains originally c_o mEq/50 ml oxalate, being 1 mEq (OX) = $\frac{1}{2}$ mM (OX), it contains

$$\frac{1}{2} \quad \frac{1}{50} \quad 10^{-3} \text{ N } c_o \quad =$$

$$= \quad 6.02 \times 10^{18} \; c_o \text{ molecules/g}$$

If the dosimeter is linear between c_o and $(1-f)c_o$ *) the number of molecules destroyed per gram, when the concentration is fc_o, is

$$6.02 \times 10^{18} \; fc_o \text{ molecules/g}$$

G being the number of molecules destroyed per 100 eV, and being 1 rad = 6.24×10^{13} eV/g, the number of molecules destroyed per rad is

$$6.24 \times 10^{11} |G|$$

*) $$f = \frac{c_o - R_a}{c_o}$$

$$R_a = (1-f)c_o$$

The dose absorbed is then

$$D_f = \frac{6.02 \times 10^{18} \; f \; c_o}{6.24 \times 10^{11} |G|} \text{ rads}$$

$$= 9.7 \frac{f \; c_o}{|G|} \text{ M rads}$$

From this equation we calculate the G-value for the oxalate destruction (whence the minus sign) as:

$$G = - 9.7 \; fc_o/D_f = - 9.7 \; (c_o - R_a)/D_f$$

For any interval of concentration sufficiently small to be considered linear we have a similar expression

$$G = - 9.7 \frac{\Delta R_a}{\Delta D} \text{ molecules/100 eV}$$

with D in Mrads, and $\Delta R_a = R_a \; (t_2) - R_a \; (t_1)$

$\Delta D = D \; (t_2) - D \; (t_1)$.

Expressing the G-value in molecular equivalents we have

$$G' = - 19.4 \frac{\Delta R_a}{\Delta D} \text{ molecular equivalents/100 eV}$$

Let us now take infinitesimal intervals. We get

$$G = 9.7 \frac{dc}{dD} = 9.7 \frac{dc}{dt} \quad \frac{dD}{dt}$$

and being $\frac{dc}{dt} = - k \sqrt{c}$, and $\frac{dD}{dt} = 0.2$ Mrad/sec, we get

$$G = - 48.2\ k \sqrt{c}$$
$$= - 0.16 \sqrt{c} \quad \text{molecules/100 eV}$$
or $$G' = - 0.32 \sqrt{c} \quad \text{molecular equivalents/100 eV}$$

Taking $R_{av} = \frac{1}{2} (R_a(t_1) + R_a(t_2))$ instead of an instant concentration we may write

$$\frac{G'}{\sqrt{R_{av}}} = - 0.32$$

In tables 7 and 8 are listed the G'-values experimentally obtained for the oxalate decrease of 0.1 and 0.2 N solutions. Division of these G'-values for $\sqrt{R_{av}}$ leads in fact to values that are close to the calculated constant value of - 0.32.

TABLE 7 G-VALUES OXALATE DECREASE (0.1 N STARTING SOLUTION)

IRR. TIME t_1 (sec)	0	0	375
IRR. TIME t_2 (sec)	125	250	625
$R_a (t_1)$ (mEq/50 ml)	4.92	4.92	2.52
$R_a (t_2)$ (mEq/50 ml)	4.04	3.30	1.35
ΔR_a (mEq/50 ml)	0.88	1.62	1.17
ΔD (10^6 rad)	25	50	50
G' (molecular equivalents/100 eV)	- 0.68	- 0.63	- 0.45
G (molecules/100 eV)	- 0.34	- 0.315	- 0.225
R_{av} (mEq/50 ml)	4.5	4.1	1.95
$\frac{G'}{\sqrt{R_{av}}}$	- 0.31	- 0.31	- 0.32

TABLE 8 G-VALUES OXALATE DECREASE (o.2 N STARTING SOLUTION)

IRR. TIME t_1	(sec)	o	25o	5oo	1ooo
IRR. TIME t_2	(sec)	25o	5oo	75o	1125
R_a (t_1)	(mEq/5o ml)	9.91	7.52	5.29	2.26
R_a (t_2)	(mEq/5o ml)	7.52	5.29	3.65	1.66
ΔR_a	(mEq/5o ml)	2.39	2.23	1.64	o.6o
ΔD	($1o^6$ rad)	5o	5o	5o	25
G' (molecular equivalents/ 1oo eV)		- o.93	- o.93	- o.64	- o.47
G (molecules/1oo eV)		- o.465	- o.465	- o.32	- o.235
R_{av}	(mEq/5o ml)	8.7	8.7	4.5	1.95
$\frac{G'}{\sqrt{R_{av}}}$		- o.31	- o.31	- o.3o	- o.34

For the o.1 N solution and for the beginning of the radiolysis o.34 molecules oxalate disappeared per 1oo eV. The initial G-oxalate-value for the o.2 N solution was found slightly higher (o.465).

These G'-values decrease after longer irradiation times. After 125 x $1o^6$ rad absorption a G' of - o.23 and - o.34 for o.1 and o.2 N solutions, respectively, was found for the oxalate disappearance.

4.1.2 - HIGHER OXALATE CONCENTRATIONS

4.1.2.1 - REACTION ORDER

Both the 1^{st} and the 2^{nd} R_a-values (permanganate titration of reductants in acid medium) deviate considerably from a zero order reaction. The square root of the 2^{nd} R_a-value plotted against the total dose absorbed leads up to appr. 3oo x $1o^6$ rad absorption to a straight line (fig. 7), indicating even here a o.5 order reaction. At higher conversions a somewhat higher reaction order is observed.

4.1.2.2 - G-VALUES

In table 9 are listed the G'- and the G-values experimentally obtained for the oxalate decrease of a o.4 N solution.

TABLE 9 G-VALUES OXALATE DECREASE (o.4 N STARTING SOLUTION)

IRR. TIME t_1 (sec)	o	1ooo	15oo
IRR. TIME t_2 (sec)	25o	15oo	25oo
R_a (t_1) (mEq/5o ml)	2o.35	11.8o	8.25
R_a (t_2) (mEq/5o ml)	17.6o	8.25	1.1o
ΔR_a (mEq/5o ml)	2.75	3.55	7.15
ΔD ($1o^6$ rad)	5o	1oo	2oo
G' (molecular equivalents/ 1oo eV)	- 1.o7	- o.69	- o.69
G (molecules/1oo eV)	- o.535	- o.345	- o.345
R_{av} (mEq/5o ml)	19	1o	4.7
$\frac{G'}{\sqrt{R_{av}}}$	- o.24	- o.22	- o.32

For the o.4 N sodium oxalate solution an initial $G_{oxalate}$ value of -o.535 was found. This value decreases after longer irradiation times. Both after 2oo · $1o^6$ and after 3oo · $1o^6$ rad absorption a G of -o.345 is calculated for the decrease in oxalate.

4.2 - PRODUCT FORMATIONS FROM o.4 N OXALATE SOLUTIONS

4.2.1 - TOTAL DECREASE OF CARBOXY GROUPS

From the H_t-values of table 6 of the acid-base titrations the total of carboxy groups in solution can be calculated. The following equations apply:

$$n(\text{-COOH}) = 2\ C_o - H_t \quad (\text{mEq/5o ml}).$$

4.2.2 - CARBOXY GROUPS BEING TRANSFORMED INTO CARBON DIOXIDE AND NEUTRAL SUBSTITUENTS, RESPECTIVELY

The equivalents of free carbonate (carbon dioxide) formed from oxalate can be determined by acid titration of the radiolyzed solution after carbonate removal (H_f-values, table 6); the difference between the total hydroxide values (H_t-values) and the free hydroxide values (H_f-values) is due to the carbon dioxide formation during the radiolysis.

$$n\ (CO_2) = \frac{H_t - H_f}{2} \quad (\text{mEq/5o ml})$$

The number of equivalents of neutral substituents being formed from the carboxy groups of the initial oxalate can be calculated from the following equation:

$$n\ (C_{neutral}) = 2\ c_o - n(\text{-COOH}) - n(CO_2) \quad (\text{mEq/5o ml})$$

$$= H_t - \left(\frac{H_t - H_f}{2}\right) = \frac{H_t + H_f}{2} \quad (\text{mEq/5o ml})$$

The experimental values for $n(\text{-COOH})$, $n(CO_2)$ and $n(C_{neutral})$ are tabulated in table b and graphically illustrated in fig. 8.

TABLE 1o RADICLYSIS OF o.4 N SODIUM OXALATE PRODUCT FORMATIONS

IRRADIATION TIME [sec]	TOTAL DOSE [10^6 rad]	n(COOH)	n(C-neutral) [mEq]	n(CO_2)
o	o	2o.3	o.o	o.o
25o	5o	17.1	o.35	2.85
5oo	1oo	14.5	o.6	5.25
75o	15o	12.5	o.65	7.2o
1ooo	2oo	11.2	o.6	8.55
15oo	3oo	7.9	o.5	12.o
15oo	3oo	8.o	o.6	11.8
2ooo	4oo	4.65	o.6	15.15
25oo	5oo	1.45	o.6	18.2
25oo	5oo	o.o5	o.8	19.4

Both the decrease in carboxy groups and the formation of carbon dioxide were found to be of a slightly higher than zero order. The concentration of neutral substituents reaches after app. 1oo x 10^6 rad absorption steady state conditions. The concentration of neutral substituents, having been formed from carboxy groups, is never exceeding 3% of the over-all concentration. This value is also in agreement with the results obtained from the 1^{st} and 2^{nd} R_a-values of the manganometric titrations (fig. 4). The difference between these two values gives the maximum of concentration of other reducing products than oxalic acid.

A C K N O W L E D G E M E N T

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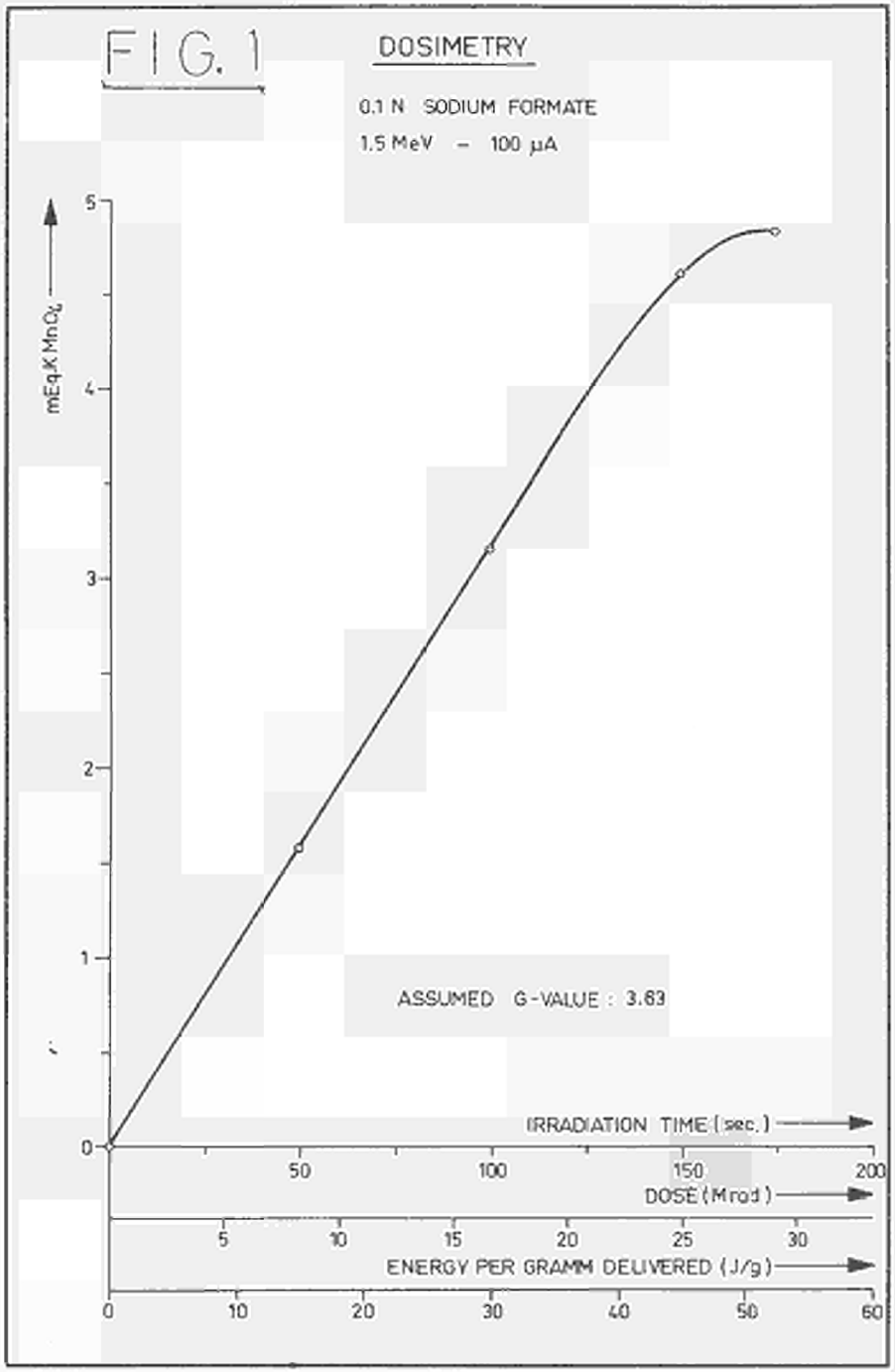


FIG. 1
DOSIMETRY
0.1 N SODIUM FORMATE
1.5 MeV – 100 µA
mEq K MnO4
ASSUMED G-VALUE : 3.63
IRRADIATION TIME (sec.)
DOSE (Mrad)
ENERGY PER GRAMM DELIVERED (J/g)

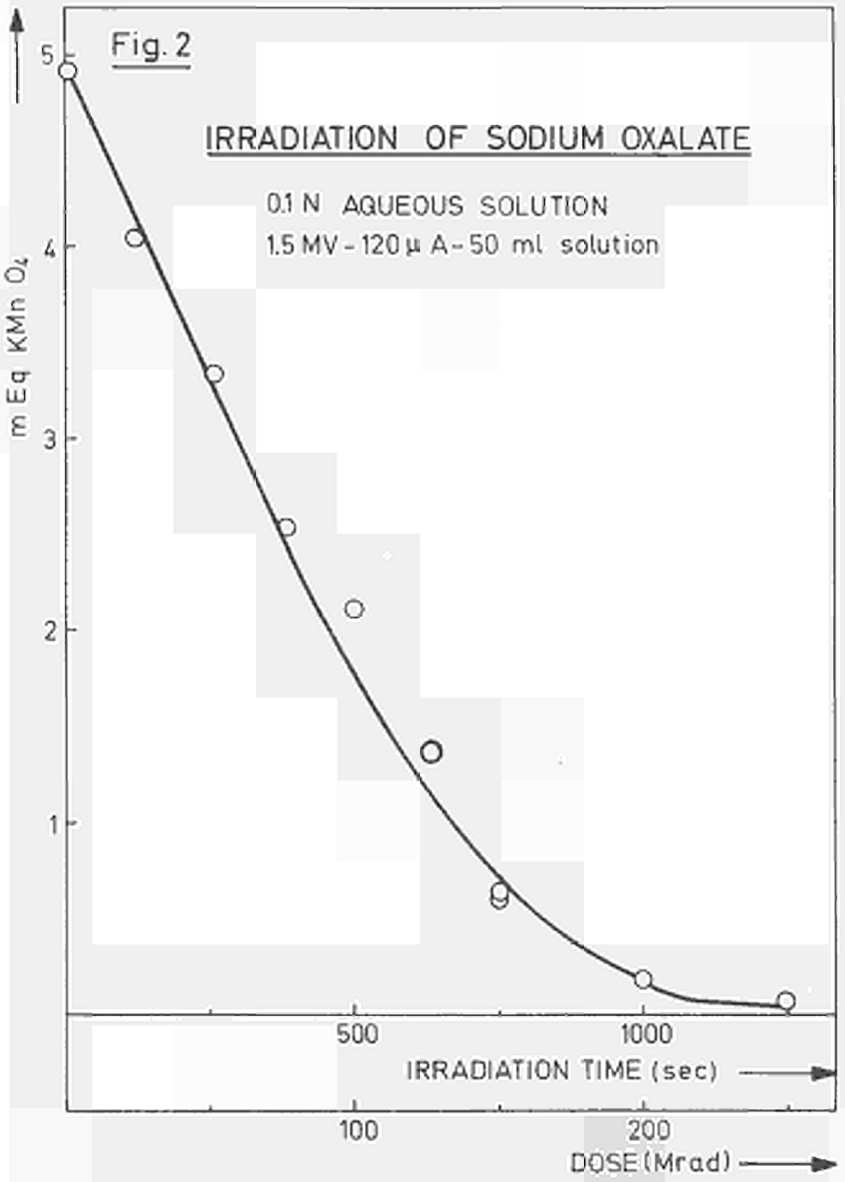


Fig. 2
IRRADIATION OF SODIUM OXALATE
0.1 N AQUEOUS SOLUTION
1.5 MV - 120 µ A - 50 ml solution
m Eq KMn O4
IRRADIATION TIME (sec)
DOSE (Mrad)

Fig.3

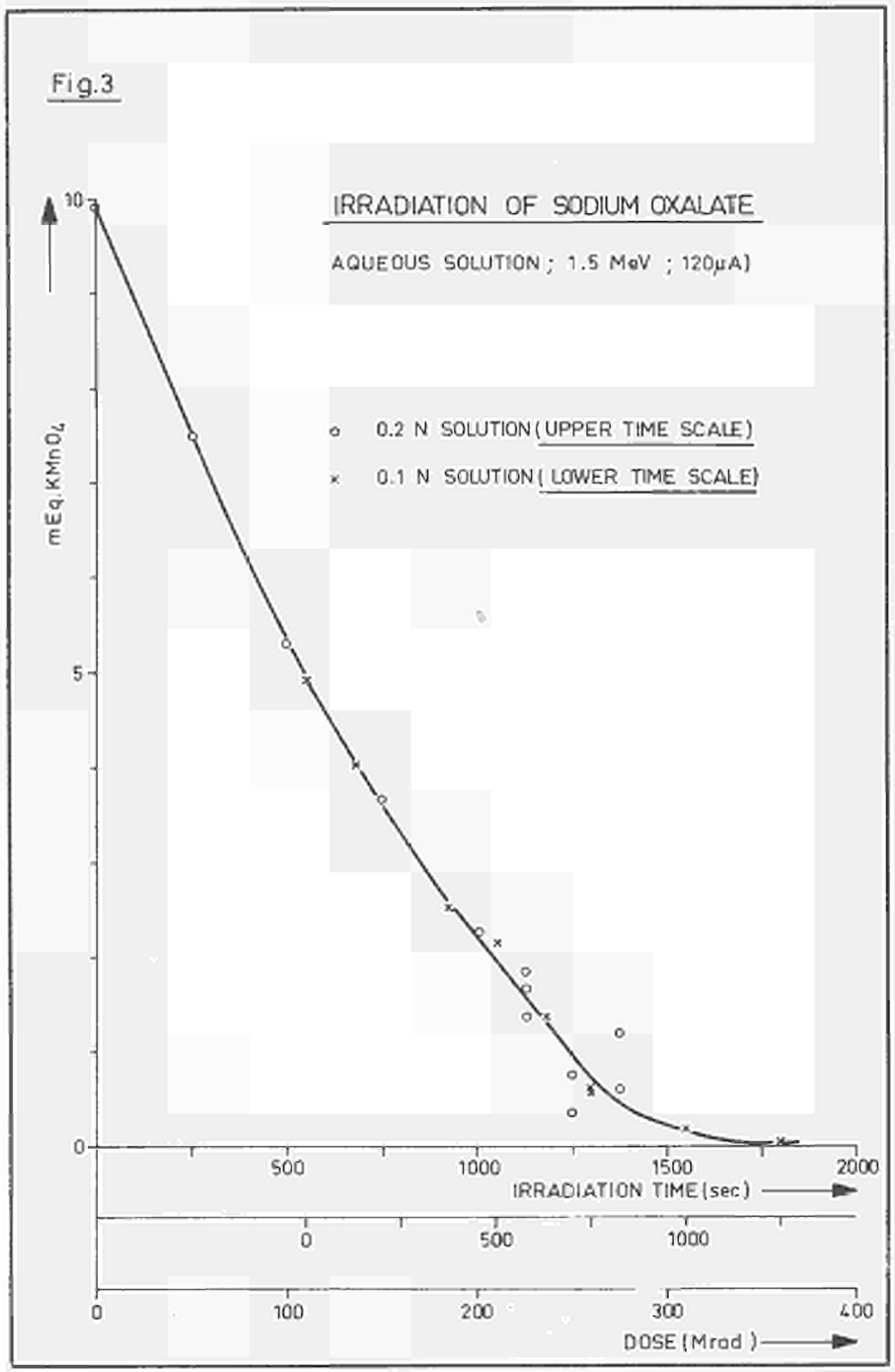
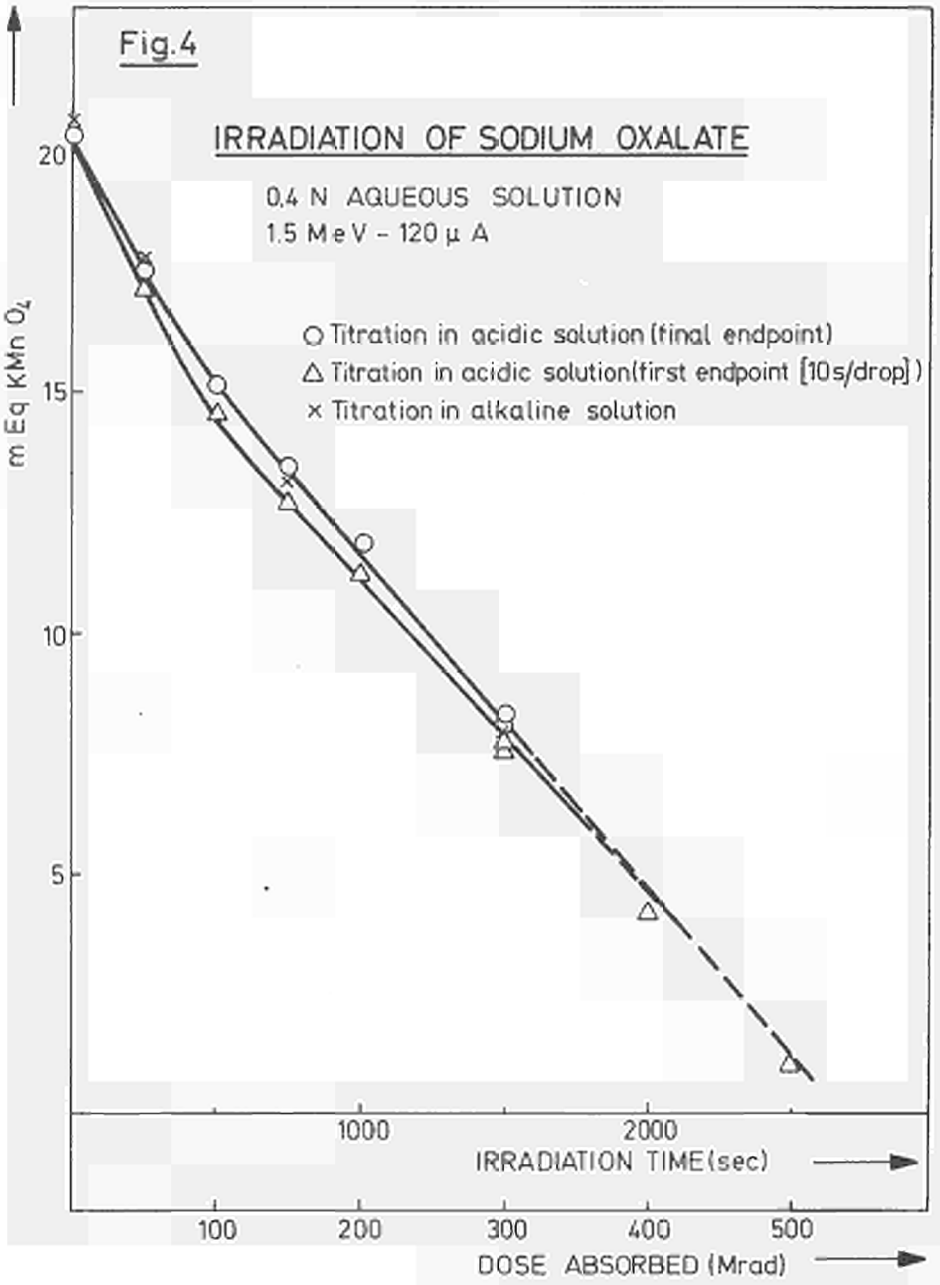

IRRADIATION OF SODIUM OXALATE
AQUEOUS SOLUTION ; 1.5 MeV ; 120μA)
o 0.2 N SOLUTION (UPPER TIME SCALE)
× 0.1 N SOLUTION (LOWER TIME SCALE)
mEq KMnO4
10
5
0
500
1000
1500
2000
IRRADIATION TIME (sec)
0
500
1000
0
100
200
300
400
DOSE (Mrad)

Fig.4


IRRADIATION OF SODIUM OXALATE
0.4 N AQUEOUS SOLUTION
1.5 MeV – 120 μ A
○ Titration in acidic solution (final endpoint)
△ Titration in acidic solution (first endpoint [10s/drop])
× Titration in alkaline solution
m Eq KMnO4
20
15
10
5
1000
2000
IRRADIATION TIME (sec)
100
200
300
400
500
DOSE ABSORBED (Mrad)

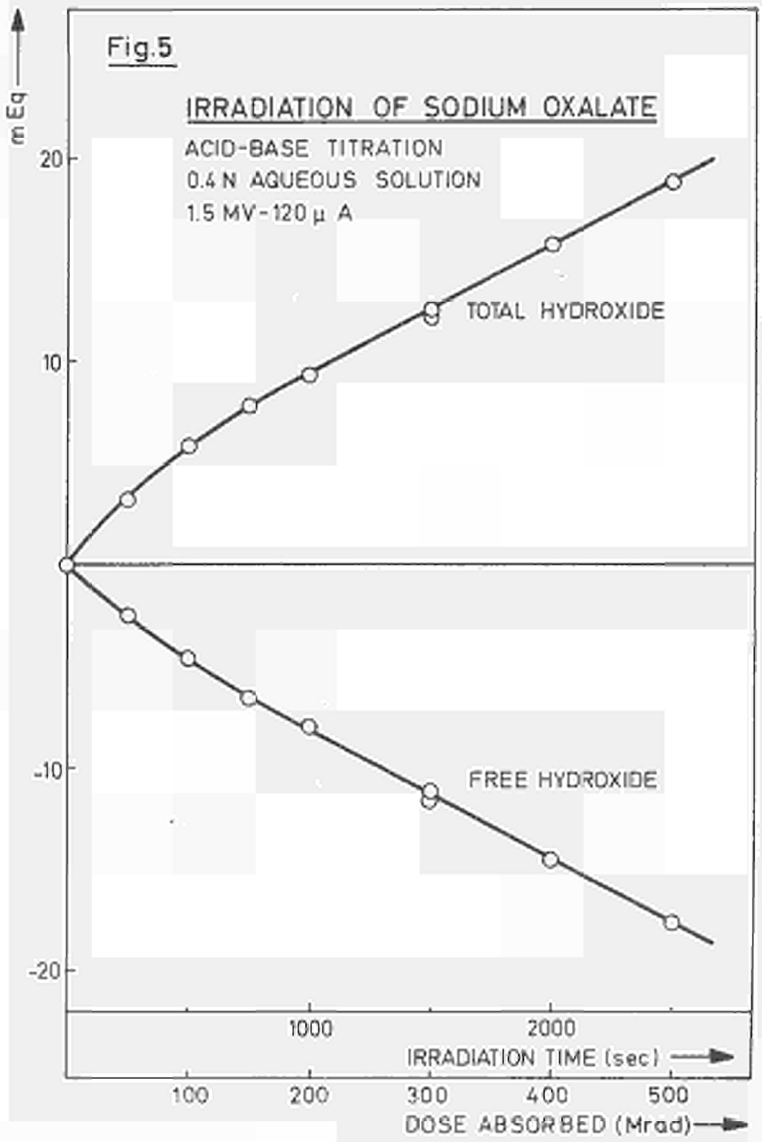


Fig.5
IRRADIATION OF SODIUM OXALATE
ACID-BASE TITRATION
0.4 N AQUEOUS SOLUTION
1.5 MV - 120 μ A
m Eq
20
10
-10
-20
TOTAL HYDROXIDE
FREE HYDROXIDE
1000
2000
IRRADIATION TIME (sec)
100
200
300
400
500
DOSE ABSORBED (Mrad)

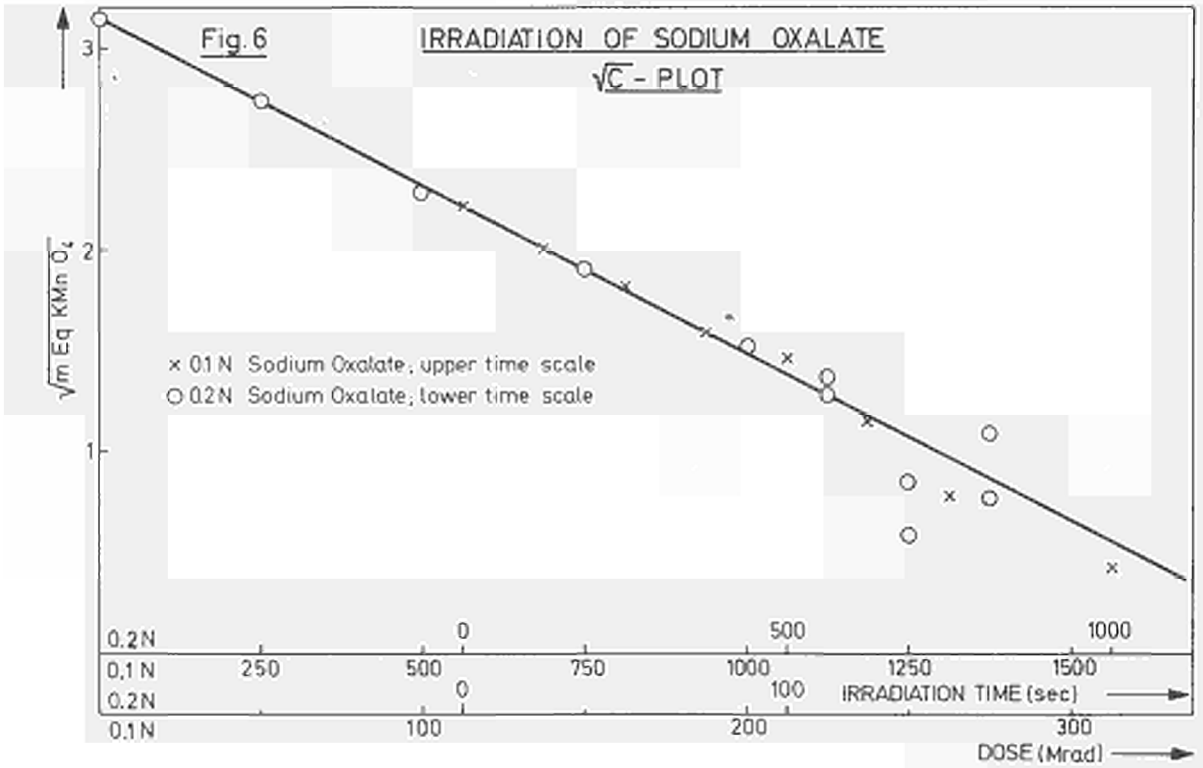


Fig. 6
IRRADIATION OF SODIUM OXALATE
√C - PLOT
√m Eq KMn O4
3
2
1
× 0.1 N Sodium Oxalate, upper time scale
○ 0.2 N Sodium Oxalate, lower time scale
0.2 N
0
500
1000
0.1 N
250
500
750
1000
1250
1500
0.2 N
0
100
IRRADIATION TIME (sec)
0.1 N
100
200
300
DOSE (Mrad)

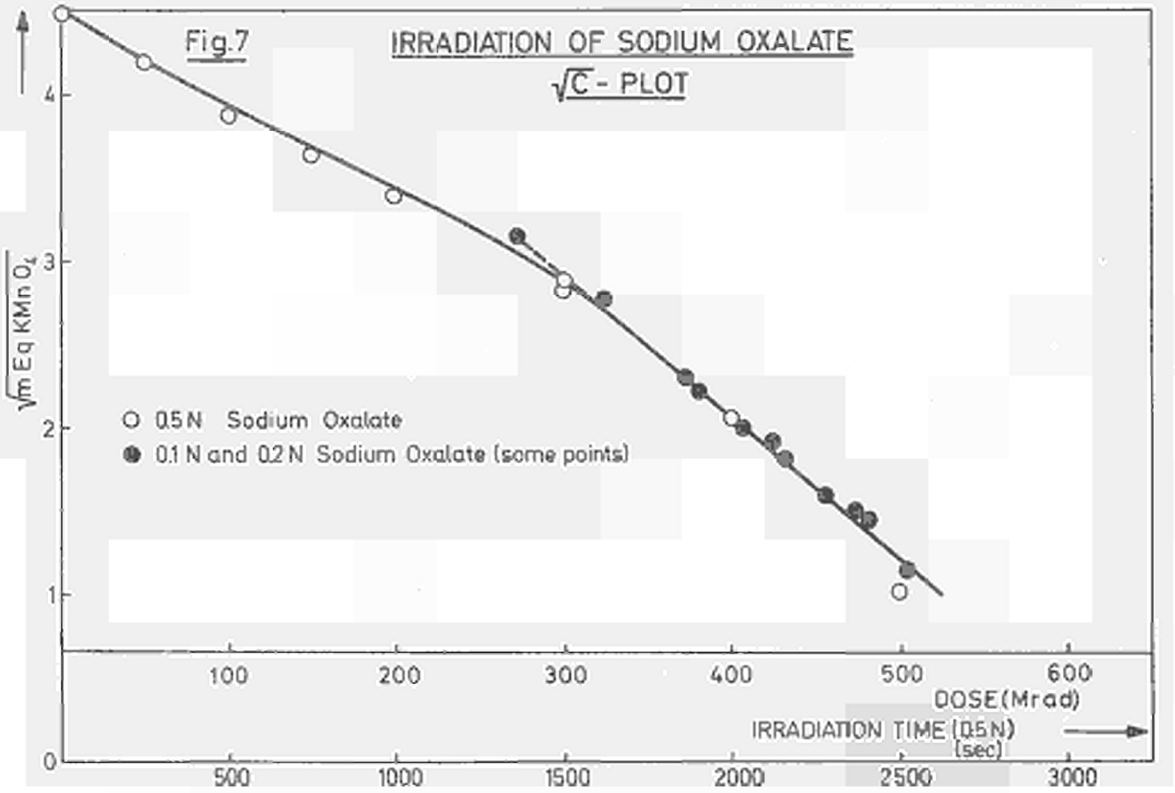


Fig.7
IRRADIATION OF SODIUM OXALATE
√C - PLOT
√m Eq KMnO4
O 0.5 N Sodium Oxalate
● 0.1 N and 0.2 N Sodium Oxalate (some points)
DOSE (Mrad)
IRRADIATION TIME (0.5 N) (sec)

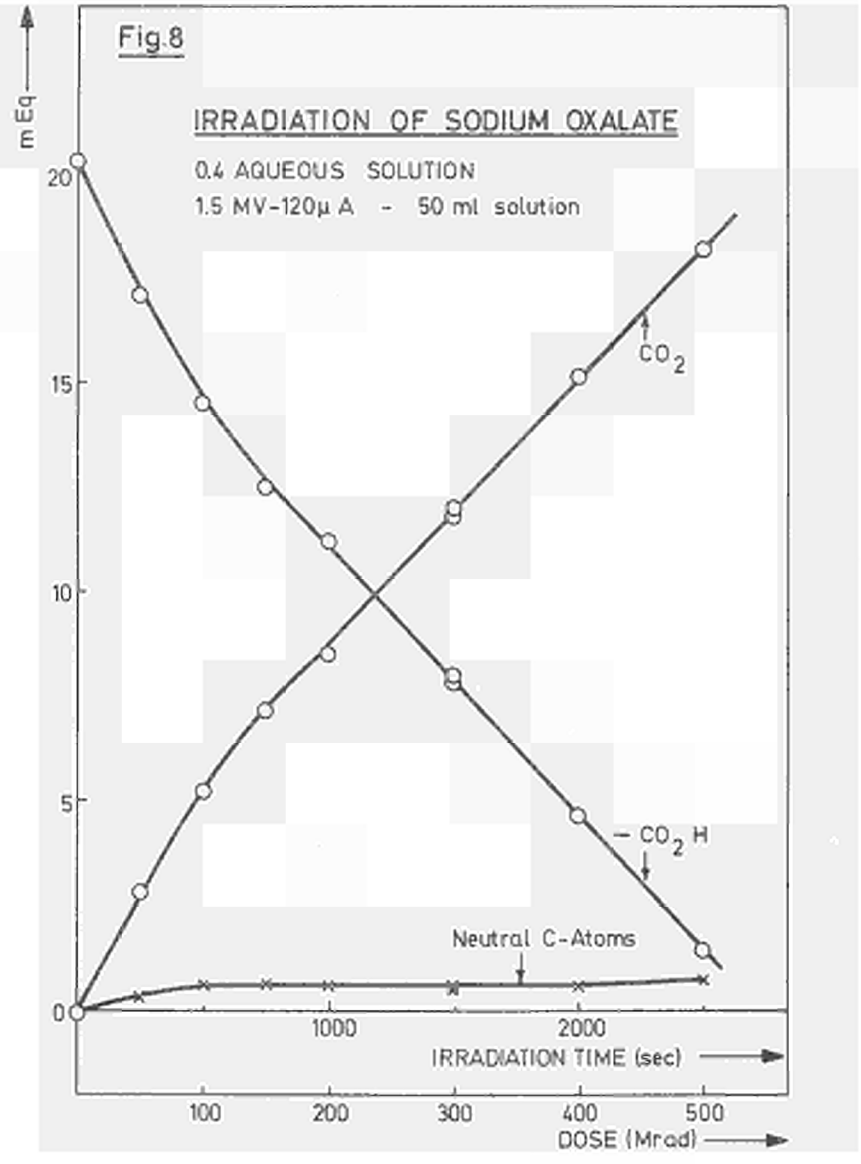
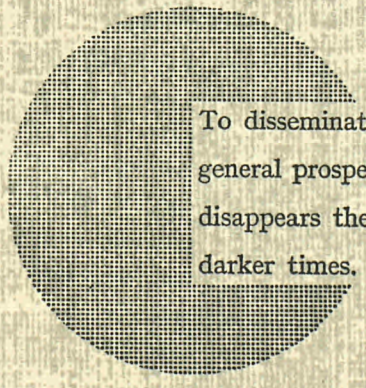


Fig.8
IRRADIATION OF SODIUM OXALATE
0.4 AQUEOUS SOLUTION
1.5 MV-120µ A - 50 ml solution
m Eq
CO2
- CO2 H
Neutral C-Atoms
IRRADIATION TIME (sec)
DOSE (Mrad)



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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